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Plating processes on aluminum and application to novel solar cell concepts

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Abstract

In this work, aluminum as contact material with low transfer resistance to p- and n-silicon is combined with the zincate process which enables plating on aluminum. In this way the excellent contact quality of aluminum and the high conductivity of plated layers are combined. Examples of application are given on two solar cell concepts. One is the both side aluminum contacted concept suitable for *p*-type and *n*-type base material. The double sided metallization approach is called DACAPO (Double sided Aluminum Contacted And Plated Overcoating) process. On *p*-type wafers, satisfactory results are shown for the metallization in terms of contact geometry (contact width down to 50 μm). Challenges of the approach such as laser and inkjet alignment and resist stability in aluminum etching solution, are discussed. Calculations of V_{OC} and R_C in dependence of the contact area show the potential of the DACAPO process for high efficiency solar cells. The second solar cell concept tested with zincate and plating is the IBC (interdigitated back contact) concept. Different possibilities of plating processes on both polarities are discussed in this context. Thickening the aluminum/silicon layer by plating results in an increased FF by 1.3 % and consequently in higher cell efficiency up to 20.4 %, even on small sized solar cells. The constructed metal stack is characterized by SEM-EDX analyses.

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1. Introduction

Aluminum is the most abundant metal in the earth crust and it has been used in solar cell metallization for a long time especially because of its cheapness and excellent electrical properties. Besides the relatively good electrical conductivity, aluminum forms a low-resistivity contact to *p*- and *n*-doped silicon [1]. A further advantage of aluminum is its reflection property, which is particularly fundamental for IBC solar cells. Therefore evaporated aluminum is often used as rear side contacting material in high efficiency solar cells. In most cases it is used as rear side metal for boron doped silicon [2, 3] but also for phosphorous doped silicon [4, 5]. It is also possible to build a both-sided aluminum metallized solar cell resulting in high cell efficiencies shown by ISFH [6]. In this case aluminum acts as contacting material and also provides the lateral conductivity where a thick evaporated layer of aluminum is required. This approach entails long-lasting etching processes for front side structuring and makes cell connection by standard soldering methods impossible. A possibility to overcome such problems is the DACAPO process which only needs a thin layer of aluminum as contact material and utilizes plated layers for lateral conductivity and solderability. On such both-side contacted cells, the ability of Al to contact both polarities is exploited.

In case of IBC solar cells a single aluminum layer can be used as contact for both silicon polarities. Commercial processes are relatively expensive because several sputtered layers are necessary [7]. A low-cost alternative is to generate only one thin evaporated aluminum layer which is electrochemically thickened to reach sufficient lateral conductivity. This approach is demonstrated in this work resulting in an increase of *FF* and consequently efficiency already on small size 20 x 20 mm² IBC cells, where lateral conductivity is less critical.

The zincate process is the essential process which combines the good contact and reflection properties of aluminum and the excellent conductivity of plated layers. The process overcomes the passivity of the aluminum surface where a native oxide layer is instantly formed in oxygen containing environments, which makes electrochemical deposition difficult [8]. In this immersion process an exchange reaction between aluminum of the PVD-layer and zinc of the solutions takes place. That results in a well adherent zinc layer which is the seedlayer for further plating of nickel, copper or silver. The process is applied on IBC cells as well as on both-side metallized *p*-type solar cells which are represented schematically in Fig. 1.

2. Experimental

There are two different materials used in the experiments. For the DACAPO process industrial 156 x 156 mm² *p*-type Cz wafers featuring a random pyramid texture, a shallow 90 Ω/sq emitter on the front side and a SiN_x anti-reflection coating (ARC). The metallization process is applied on two cell batches. The first batch was planned as first demonstration of the both sided process. Due to this no passivation was used on the rear side. After finishing the first batch, the second batch is started in order to prevent some challenging processes which takes place in the first batch. One optimization was the rear side passivation. Therefore the cells of the second batch are equipped with a passivation stack of 10 nm AlO_x and 90 nm SiO_x. These wafers have been metallized with the DACAPO process sequence as shown in Fig. 2. After the LFC-process, several wafers were diced into 50 x 50 mm² samples in order to increase sample quantity for zincate and plating variations (processes framed by red rectangle).

For the second approach of plating IBC solar cells, 20 x 20 mm² samples as described by Keding [9] were used. The solar cells consisting of Cz silicon material have a thickness of 170 μm and a base resistivity of 6.1 Ωcm. PVD aluminum containing 1 % silicon is used as contact material. In this case the PVD layer is relatively thick (about 3 μm) which is not necessary but neither adverse for the zincate process. The aluminum is structured by a masking and etching process. The zincate process is the same as described in an earlier publication [10]. In this work, some plating variations and an EDX analysis are done additionally. One route is to plate silver on top of the zincated aluminum layer and the other more cost-efficient route is to plate nickel and copper on top of the zinc covered aluminum.

The used zincate as well as the plating solutions are commercially available. The produced stack of metals is characterized by SEM-EDX analysis.

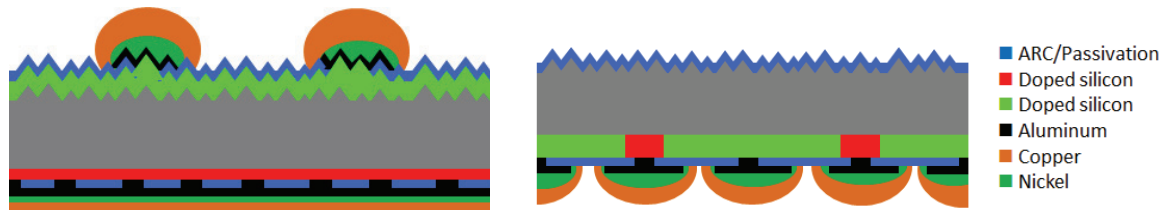


Fig. 1. Schematic drawing of double sided contacted solar cell (left) and IBC solar cell (right).

3. Both side aluminum contacted approach

3.1. Process sequence

At first sight the DACAPO process looks extensive but it should be noted that most processes run double sided. Additionally most processes are short and using low cost materials. Some processes like laser fired contact (LFC) formation are needed in any comparable process sequence and are no additional steps in the DACAPO sequence. The first process step is the laser ablation of the front side ARC which is followed by PVD deposition of a thin aluminum layer on both sides. In this experiment the deposition takes place on front and rear side successively. In case of an industrial process it is also imaginable to do the deposition on both sides at the same time to shorten the deposition time. The next step is the printing of a resist by inkjet or screen printing. In the present experiment, the resist is printed by inkjet on both sides because the next step was etching of aluminum which is not single sided in our lab setup, but can be arranged to be single sided in an industrial process. This would save the resist for the rear side and make the sequence less costly. Because p -type precursors were used in this experiment, a LFC process was employed for building up a BSF (back surface field). This process step would not be necessary when using n -type base material. To increase the lateral conductivity of front and rear side metal the zincate and plating processes are done. Detailed information about the process steps which are working simultaneously on both sides are shown in section 3.3.

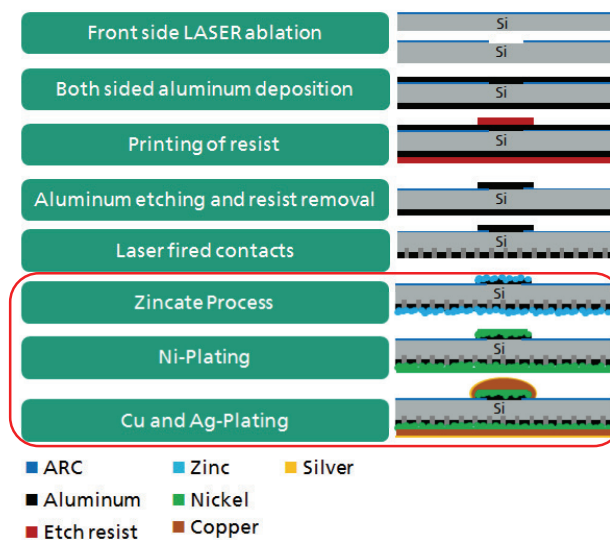


Fig. 2. Process sequence of the DACAPO process for p -type solar cells.

3.2. Laser-inkjet-alignment

One big challenge of the overall process is the alignment of the front side resist printing process to the laser process for ARC opening. The inkjet resist of the front side has to cover the entire ablated area so that it is completely covered by the PVD aluminum pattern after Al etching. In a first batch only relatively wide contacts were achieved, because the printed resist layers are about 100 μm wide, which in the end results in plated contacts of 120 μm . It should be noted that despite the large contact width, the contact area is very small due to narrow laser ablation (even non-continuous point contacts are possible), which is one of the strengths of the DACAPO sequence. After further alignment tests narrow inkjet lines about 50 μm could be printed in a second run which covered the 20 μm opened lines homogenously over the whole area of 156 x 156 mm^2 . A laser microscopic picture of the inkjet line and opened line of the second batch is shown in Fig. 3. On the one hand those small printed inkjet lines result in relatively small contact fingers but on the other hand the etching process can be problematic. If the resist line is narrow, it could result in adhesion problems if the resist is not optimized on the aluminum etching solution. This can lead to line interruptions. The adhesion during the etching process is improved by reduction of the etching solution temperature and the abandonment of agitation.

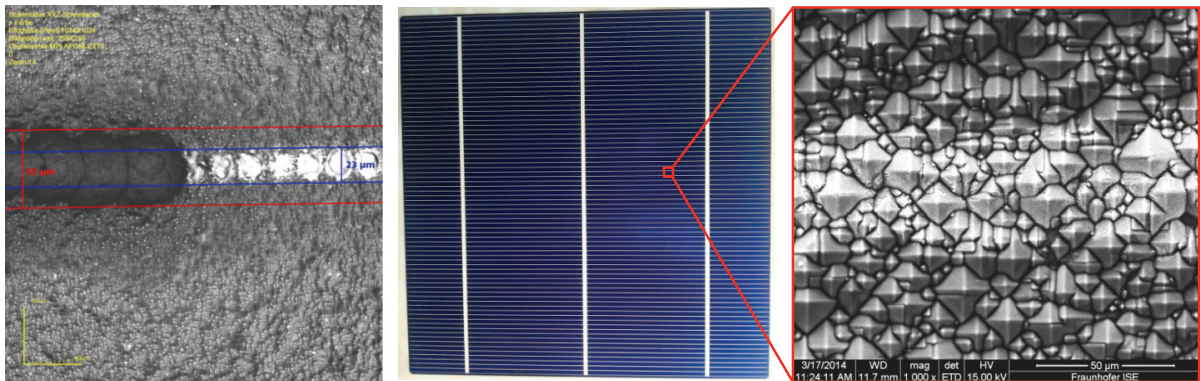
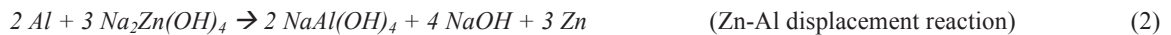


Fig. 3. Left: Microscopic picture of inkjet resist on laser ablated area for alignment tests. Middle: Picture of aluminum pattern after structuring by mask and etch. Right: SEM image of aluminum seed layer.

3.3. Zincate and plating

After resist stripping there is an aluminum pattern on the solar cell front side and full area aluminum on the rear side. Because of the self-passivation property of aluminum by building up a natural oxide layer it is not possible to plate on it by standard electrolyte solutions. For this reason the zincate process, which has already been a standard in automotive and electrical industry for a long time, is applied. There are alkaline as well as acidic commercial zincate solutions available. As alkaline solutions have proven to be reliable in terms of adhesion in the past [10], such a solution was used in the present experiment. The strong basicity induces a chemical attack of the natural oxide layer on the aluminum. As soon as the oxide layer is etched away the displacement reaction of zinc and aluminum takes place. Zinc, which is a component of the zincate solution, is deposited while aluminum is dissolved into the solution due to its higher electrochemical standard potential. The reactions that take place at the aluminum surface are shown in equations 1 and 2.



The zincate process is no galvanic deposition process but it is a chemical immersion process in which the sample is fully dipped into the solution. In case of the double side metallized sample the deposition takes place simultaneously on front and rear side. For sufficient adhesion of the deposited layer a double zincate process is necessary. The first roughly crystalline deposited zinc layer is etched away by nitric acid. The second deposited zinc layer is more dense and microcrystalline shown in [10]. Due to the first zincate process the aluminum is etched which results in an increased aluminum surface. This is the base for a homogeneous zinc layer formed by the second immersion. The altogether double zincate process is very fast and takes only below one minute. The next process step is nickel plating which has been demonstrated by chemical or electrochemical plating. In this approach a commercial chemical nickel electrolyte is used to get good homogeneity over the whole area. This process is also short because it is not necessary to plate a thick nickel layer. The lateral conductivity that is necessary for a working solar cell is ensured by the following plated copper layer. In order to get sufficient conductivity, about 10-15 μm copper is plated by electroplating.

In case of IBC solar cells, both *p*- and *n*-busbar are usually contacted directly for copper plating. In case of the double side contacted solar cells there are several possibilities of plating both polarities simultaneously. One possibility is to contact the front and rear side directly. In our case of a *p*-type solar cell with phosphorous front emitter it is also possible to plate the front side by LIP (light induced plating) which makes connection of the narrow front side features needless. This route was followed in the present experiment. In this way it is possible to adjust the plating parameters to get the desired copper deposition on front and rear side simultaneously.

The evolution of front side copper contact formation is shown by SEM images in Fig. 4.

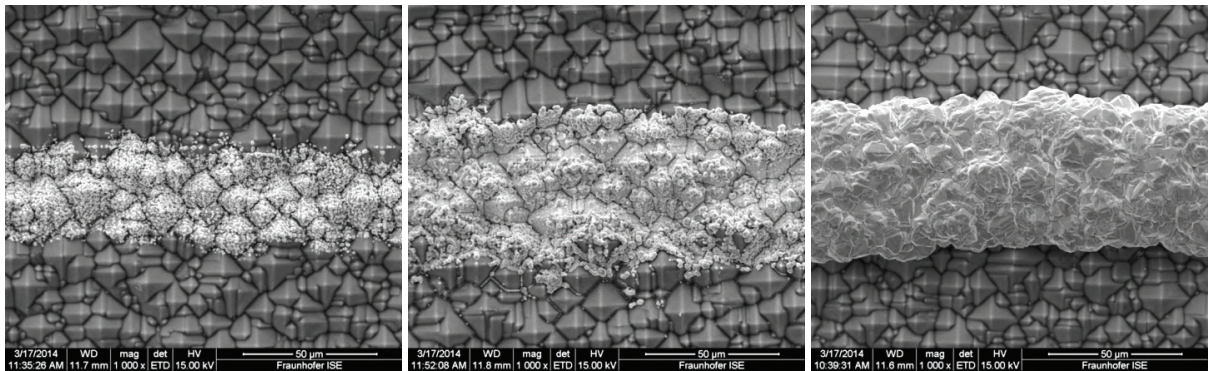


Fig. 4. SEM images of contact fingers after zincate process (left), after nickel plating (middle) and after copper plating (right).

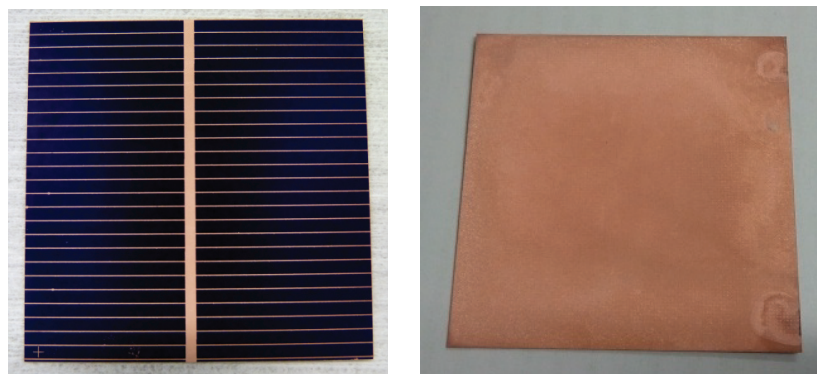


Fig. 5. Photographs of rear and front side of double side processed cell after zincate process and nickel-copper plating.

3.4. Electrical results

The main goal of the experiment is to demonstrate the performance of the DACAPO process regarding the zincate and plating process that should result in narrow front side lines. Both low contact resistance and high lateral grid conductivity need to be achieved. Additionally, an electrical characterization of the cells may give hints regarding possible challenges of the process sequence. In that respect, especially the pFF gave interesting insights. The V_{OC} potential is shown in light IV measurements resulting in V_{OC} values around 565 mV for the first cell batch and around 615 mV for the second cell batch. Pictures of rear and front side of a processed cell are shown in Fig. 5. The cells of the first batch result in very low V_{OC} values because there is no passivation layer on the cell rear side. Additionally, the resulting plated fingers are relatively wide up to 120 μm in the first cell batch which leads to low J_{SC} values. Only the FF of 77.3 % is acceptable in this batch. We tried to eliminate the mentioned problems for the second cell batch. By using an additional passivation layer of AlO_x and SiO_x the V_{OC} is increased to 616.6 mV for the best cell. The optimized front side metallization with finger widths of about 50 μm after plating (Fig. 4 right) results in a higher J_{SC} (38.67 mA/cm^2). Nevertheless the cell efficiency of the processed cells of the second batch is quite low. The main reason for this is the limited FF due to shunting. Measured pFF is only about 75.5 %, most probably due to aluminum spiking at the front side. The emitter of the cells used in the second batch is too shallow for the chosen thermal aluminum evaporation, where temperatures of $\sim 400^\circ\text{C}$ can be reached at high deposition rates.

Table 1. IV-Results of processed p -type cells by DACAPO process.

IV-Results of the best 25 cm^2 cells	V_{OC} (mV)	J_{SC} (mA/cm^2)	pFF (%)	FF (%)	η (%)
1 st Batch	564.3	34.36	80.9	77.3	15.0
2 nd Batch	616.6	38.67	74.5	71.6	17.1

There is a lot of place for optimization for a following batch. Most important is preventing aluminum spiking by using a deeper emitter, lower the deposition rate of Al deposition or by changing the deposition technique (e.g., e-gun evaporation). Also, Al-Si can be employed instead of Al. Another optimization potential lies in the reduction of the opened ARC area on the front side which is about 2.3 % of the whole area in the second batch. In this way the V_{OC} could be increased. However, especially for the case of the discussed p -type solar cell structure, care needs to be taken not to overshoot contact area reduction. Besides rising V_{OC} , also the contact resistance increases dramatically below a certain contact area fraction, as discussed in the following.

3.5. Results and calculation for n -type wafer

Making some assumptions about an ideal contact structure, one can calculate the potential of this approach on p - and n -type silicon. Values of $1.43 \times 10^{-12} \text{ A}/\text{cm}^2$ for J_0 and $3.9 \times 10^2 \text{ A}/\text{cm}^2$ for J_{SC} are assumed. The calculation is done for passivated cells of n - and p -emitters with different front side contact opening areas from 0.5 to 5.0 % (Fig. 6). The contact resistance values are taken from Schroder et al [1], assuming a surface concentration of $1 \times 10^{19} \text{ cm}^{-3}$ to phosphorous-doped and boron-doped silicon. These assumptions are realistic for high-efficiency solar cell concepts. Using laser techniques for ARC ablation, contact openings of 10 μm width are realizable. The voltage potential can be increased by about 10 mV by reduction of the opened contact area. However, at the same time contact resistance rises especially in case of an n -type emitter (solid red line Fig. 6). Contact resistance on boron emitters is negligible in all cases (dashed red line Fig. 6).

In summary, the DACAPO process is most interesting for high efficiency solar cell concepts, especially using boron emitters. Next steps will be the demonstration of the process for n -type wafer of high efficiency potential.

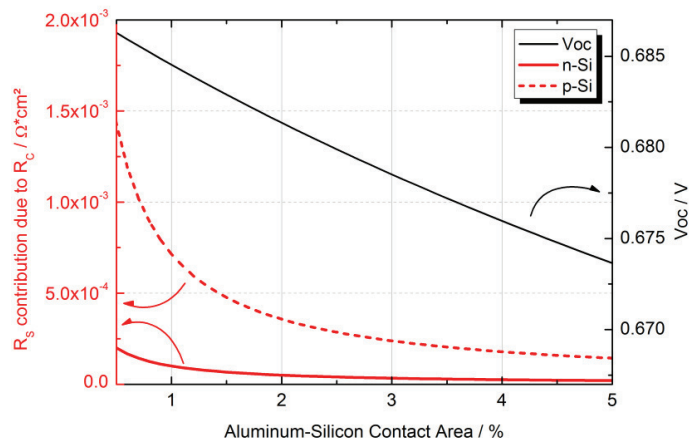


Fig. 6. Calculation of the influence of contact area on V_{oc} and R_c of n - and p -silicon.

4. Metallization process for IBC cells

4.1. Zincate and plating

Due to the fact that commercial IBC solar cells are metallized by PVD aluminum or aluminum/silicon, the zincate and plating process is of particular interest in this case. The zincate process with subsequent nickel and copper plating in one approach and with subsequent silver plating in another approach is applied on small area 20 x 20 mm² IBC cells. The former approach is interesting for long IBC cells with long contact fingers and busbars at the rim, while silver is only interesting for other rear side architectures that require lower layer thickness due to costs. If copper is deposited, an electroless nickel electrolyte is used in order to deposit a thin diffusion barrier layer after the zincate process. Copper or silver are deposited by electroplating. There are several possibilities of plating both polarities at the same time. The easiest way is to contact each polarity directly, giving the best control of the plated layer growth. Another possibility is to contact only the seed layer on the n -silicon and utilize the diode property of the solar cell which results also in plating of the p -silicon seed layer. A third approach is to contact only the p -silicon seed layer to plate directly on it and induce plating on the n -silicon seed layer by light irradiation of the front side. The selection of approach depends on which PVD electrode can be contacted easiest and on possible resistivity constraints for the chosen rear side architecture.

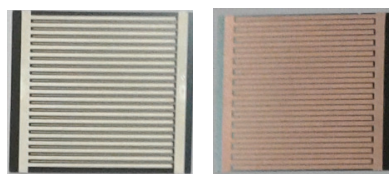


Fig. 7. Photographs of IBC cells processed by zincate and silver respectively copper.

4.2. Electrical results and cross section analysis

In case of the described IBC cells the FF was slightly limited by the lateral conductivity of the aluminum metallization. Through the implementation of the zincate process and plating, the FF is increased significantly for both plating approaches which are shown in Fig.7. The FF of nickel and copper plated samples increased by 1.4 % and the FF of silver plated samples by 1.3 % resulting in a FF of 79.4 %. Consequently the solar cell efficiency

increased by 0.6 % to an absolute efficiency of 20.4 %. The IV values of the best cell before and after applied zincate and plating process are shown in Table 2.

The difference in performance increase of the nickel and copper plated cells to the silver plated cells is not caused by the plated material but by the quantity of the plated metal. Consequently an additional plating step would further increase the FF.

Table 2. IV-Results of IBC solar cells before and after zincate and plating process.

IBC solar cell	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	Eta (%)
Before plating	627.5	40.46	78.1	19.8
After zincate and silver plating	628.5	40.82	79.4	20.4 ¹

¹ measured by Fraunhofer ISE call lab PV cells

The metallized stack of a cell of the best performing process by silver plating was analyzed by an SEM-EDX investigation that is shown in Fig. 8. It becomes apparent that the aluminum/silicon (AlSi) is etched by the highly alkaline zincate solution. The etch pits in the AlSi act as anchor points for the deposited zinc and consequently yield excellent adhesion.

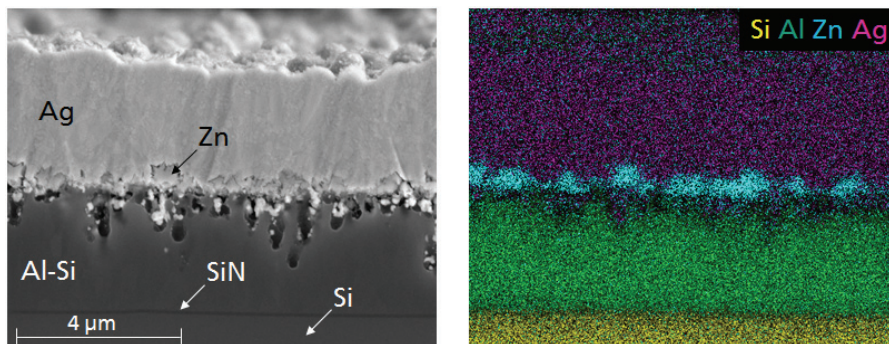


Fig. 8. SEM-EDX analyses of deposited Al-Si/Zn/Ag stack on IBC solar cells.

5. Conclusion and outlook

A process sequence for the double sided metallization of solar cells based on evaporated aluminum or aluminum/silicon and subsequently plated contacts has been introduced. The so-called DACAPO process has been applied on *p*-type solar cell structures resulting in contact lines of excellent geometry and adhesion. The advantages and also the challenges of the process are discussed. Especially the temperature during the Al deposition process needs to be adjusted to the emitter design in order to increase efficiency. In principle, the structure allows excellent contact resistance and V_{OC} results, as has been shown by calculations. The calculation reveals that the V_{OC} can be increased by ~10 mV for the assumed cell structure by reducing the contact area. Simultaneously, the contact resistance to *n*-doped silicon increases significantly, while this issue is negligible for the contact to *p*-doped silicon. This makes the process most interesting for high efficiency *n*-type solar cells with *p*-doped front side emitter.

The zincate process which makes electrochemical deposition on aluminum possible in the first place, has also been applied on IBC solar cells. This leads to an improvement of *FF* because the lateral conductivity is increased by the plated layers. The resulting metal stack has been characterized by SEM-EDX analyses.

Looking ahead it will be exciting to apply the zincate process on high efficiency potential *n*-type wafer and to make economical calculations regarding the approximate process costs on industrial scale.

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